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Review Article

Impedance spectroscopy of battery cells: Theory versus experiment

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Abstract

Electrochemical impedance spectroscopy (EIS) is an accurate electrochemical method able to identify various electrochemical steps that occur in complex electrochemical systems such as battery cells. In order to extract the maximum information from given battery system, systematic experiments that combine EIS with other (complementary) techniques are needed, as reported occasionally in the recent literature. Additionally, a proper quantitative evaluation of measured spectra has to be based on physical models which, however, tend to be quite elaborate and frequently less accessible to the wide battery community. In various cases of practical interest, however, the models can be simplified as shown in this review. One level of simplification reduces the full solution to the well-known de Levie model and is frequently used for description of the effects of porous electrodes. The ultimate level of simplification, in turn, leads to a Randles-like equivalent circuit for each insertion electrode and a pure resistor for the electrolyte phase in separator. This review shows that care has to be taken when using these simplifications in order to keep the analysis consistent and physically sound.

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Batteries, Impedance spectroscopy, Physics based modeling, Equivalent circuits..

Introduction

In order to improve the performance of batteries (power density, durability, etc.), a better understanding of the electrochemical mechanisms taking place during their operation and storage is needed. Electrochemical impedance spectroscopy (EIS) is a non-destructive method that can give important information about the main transport and reaction steps occurring in both electrodes as well as in other cell components, i.e., current collector, electrolyte-filled separator, etc.

A potential obstacle towards more effective use of EIS is that the measured spectra are notoriously difficult to analyze in a satisfactory way. Although accurate and quite complete physical models of processes occurring in a battery cell have been known for a long time [1], authors usually avoid using the corresponding analytical solutions [2,3], [4**] or numerical methods [5**] to calculate the theoretical impedance response and compare it to the actual measurements. This is probably because both approaches are rather tedious, so one has to dedicate a significant amount of time to analyze large sets of measurements under variable conditions.

On the other hand, there does exist a much simpler and faster way to evaluate a typical EIS spectrum, i.e., the use of equivalent circuits [4**]. The main problem with the latter is that they are frequently constructed intuitively rather than derived from physical models so one may doubt about their correctness. Fortunately, since more than a decade accurate transcriptions from the standard physical models for porous electrodes (e.g., Newman's model of porous electrode [1] or Poisson—Nernst—Planck equations [6]) into transmission line models have been reported [7,8]. Even if such transmission lines are rather complex and may contain contributions of little relevance for actual battery cells, they can serve as an excellent reference point for evaluation of physical soundness of simpler, more practical circuits. This article exploits this possibility by referring to typical recent articles employing EIS in the field of batteries. As demonstrated, there are many cases of interest where simplified equivalent circuits provide excellent and physically justified description of processes in battery cells. By contrast, in some cases more elaborate circuit variants taking into account additional physical processes are needed in order to explain the special features observed in impedance spectra.

Reference circuit model: Transmission line model for porous electrodes derived from physics equations

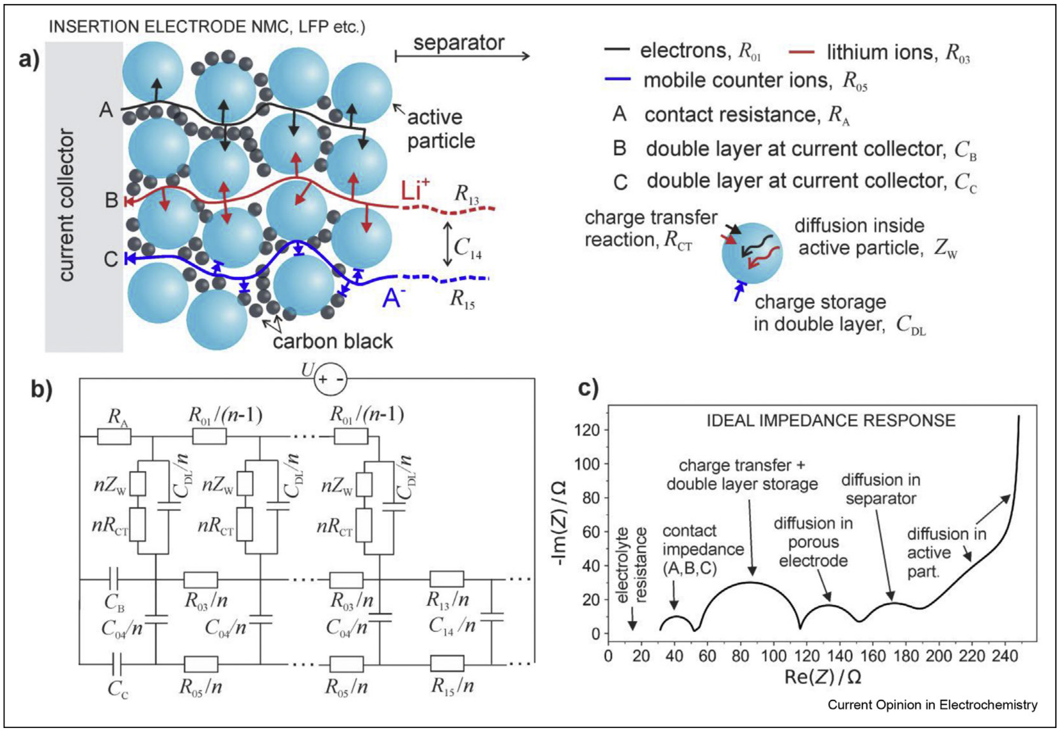
In most cases, contemporary battery electrodes are porous by nature, as schematically depicted in Figure 1a [9,10]. They consist of powdered active material (for example, particles of transition metal oxides, graphite, etc.) soaked with liquid electrolyte that contains mobile ions, both active and non-active. During battery operation, active ions and electrons move simultaneously from ionic reservoir in separator and current collector, respectively, towards active particles where they undergo electrochemical reaction and are then stored inside active particle. All these steps can be physically described using conventional models, among which the Newman's model [1] is the widest used. The latter however, can be accurately transformed into an electric transmission line [7,8]. An upgraded version of such derived transmission line is shown in Figure 1b while its general theoretical impedance response is depicted in Figure 1c.

Simplifications of the reference circuit model

In general, the reference (full) model [9,10] contains all the processes that are known or assumed to occur in a porous battery electrode, regardless of the actual storage mechanism [8]. In optimized battery cells, however, some of those processes may generate very low impedances so they can be neglected. Additionally, some of the processes that occur outside the measurement region of interest, for example at (very) low frequencies, can also be neglected. Two typical simplifications that have been most frequently used in the recent literature are shown in Figure 2b, c with typical responses shown in Figure 2f,g, respectively. The first simplification [9] is also known as the de Levie model and neglects the diffusional processes in the electrolyte phases in pores of electrode and in separator, i.e., it assumes that only the active species, for example, lithium ion in Li ion batteries, is mobile in those phases. As shown in the next chapter, such a model is appropriate in cases where the impedance due to diffusional processes is small or when the research focus is on frequencies above ca. 1 Hz.

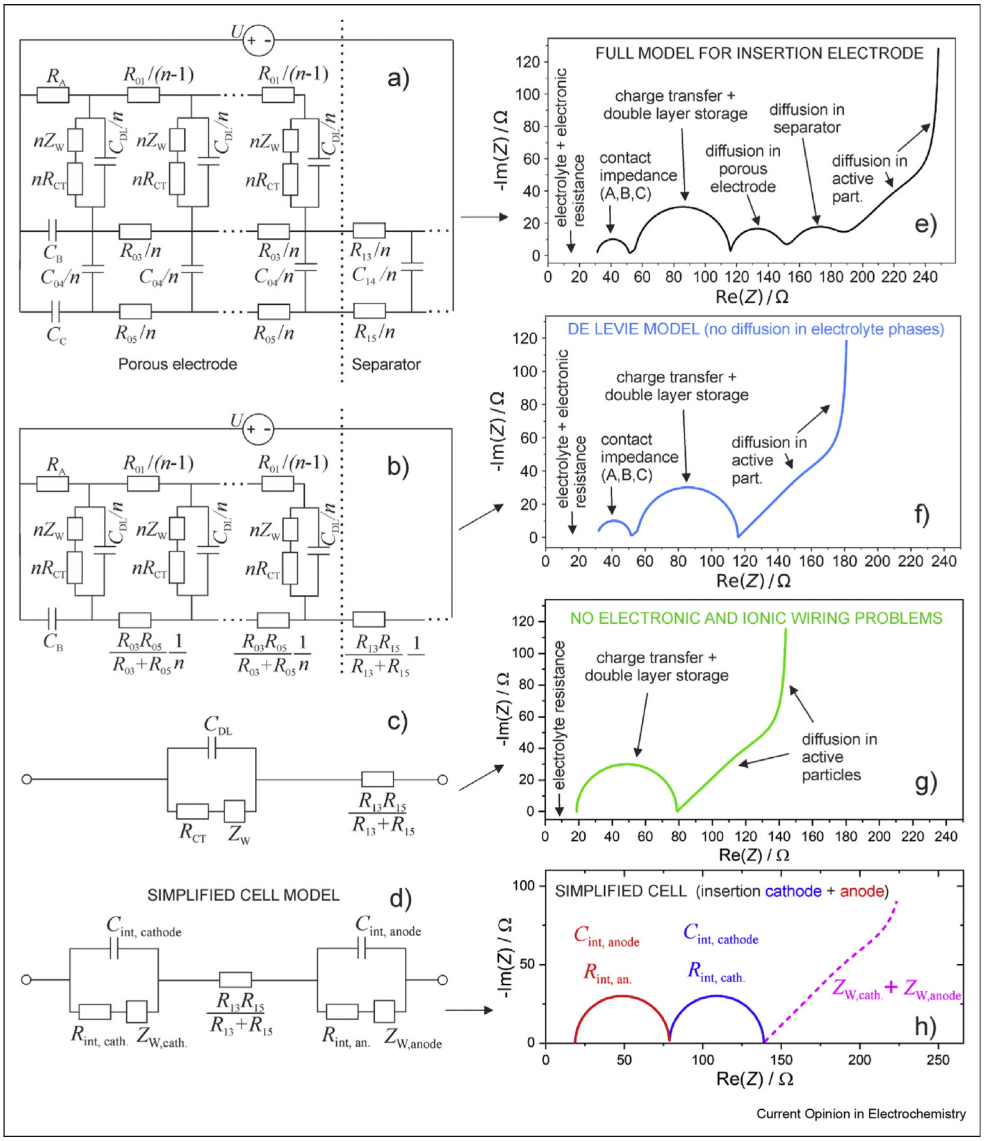
In cases, when the resistance due to movement of ions in the electrolyte in electrode's pores (R_{03}) as well as the movement of electrons across the solid conductive additive (R_{01}) can also be neglected, one ends up with the circuit and general spectrum shown in Figure 2c,g, respectively. Indeed, this circuit is frequently the basis

Figure 1



(**a**) Typical processes in a lithium-ion battery electrode and their physical meaning. (**b**) Physics based transmission line model describing processes in scheme (**a**). (**c**) General impedance spectrum generated by transmission line model in panel (**b**) (Adapted from the studies by Moškon et al. [9,10]).

Figure 2



(**a**) General physics based transmission line model for insertion electrode. (**b**) de Levie simplification of the general model by assuming that only the active species is mobile in liquid phases. (**c**) Simplification of the de Levie's model assuming that all the contact resistances, as well as the electronic and ionic wiring inside porous electrode are negligible. (**d**) Simplified model for full battery cell containing anode, electrolyte and cathode. (**e–h**) Typical impedance spectra generated by models (**a–d**), respectively.

for construction of simplified cell model containing anode, electrolyte and cathode, as shown in Figure 2d with a general spectrum shown in Figure 2h. For the sake of generality, we denote the interfacial capacitive and resistive elements $C_{\text{int,anode}}$, $C_{\text{int, cathode}}$ and $R_{\text{int,anode}}$, $R_{\text{int, cathode}}$, respectively.

In continuation we show and comment on the recent usages of the simplified models shown in Figure 2 for analysis of porous battery electrodes or cells with such electrodes.

Use of the de Levie simplification (Figure 2b, f) for analysis of impedance of porous battery electrodes

Morasch et al. [11**] used a modified de Levie model to study the impact of ionic resistance inside pores of graphite anodes on the impedance response while changing systematically the electrode thickness. Due to good electronic conductivity in such electrodes they set the corresponding parameters, R_A and R_{01}, to zero. As they only focused on relatively high frequencies (above 0.1 Hz), they could also neglect the effects of solid state diffusion by removing Z_w from the circuit. A very good agreement between the theoretically expected trends and the measured ones was reported, thus proving the suitability of the de Levie model for such analyses.

A slightly more complex variant of the de Levie model was also used for detailed study of charge-transfer in $Ni_xMn_yCo_{1-x-y}$ cathodes [12*]. In this case, the electronic resistance, R_{01}, was not neglected and the contact resistance between current collector and electrode composite R_A was also taken into account—in parallel with double layer element C_B—which formed an additional high-frequency arc. Again, the low frequency part accounting for solid state diffusion inside $Ni_xMn_yCo_{1-x-y}$ was not taken into account. Combining the EIS analysis with microscopical date, the authors were able to provide very reliable data related to the charge transfer process.

A similar de Levie type of transmission line model was successfully used for analysis of the kinetics of all-solid-state sulfur cathodes [13]. Wang et al. [14*] also used a similar variant of the model, however, with a blocking interface between the electrolyte and the active particles (using a lithium-less electrolyte). They were able to accurately determine the ionic resistance inside the pores of various cathode materials, such as cobalt oxide, nickel-manganese-cobalt oxide, lithium iron phosphate, and lithium titanate. A de Levie type of transmission line model was also used to study porous electrodes containing blended active materials [15]. The special effects due multiple types of active materials were taken into account by using a large number of parallel transmission lines with variable element values.

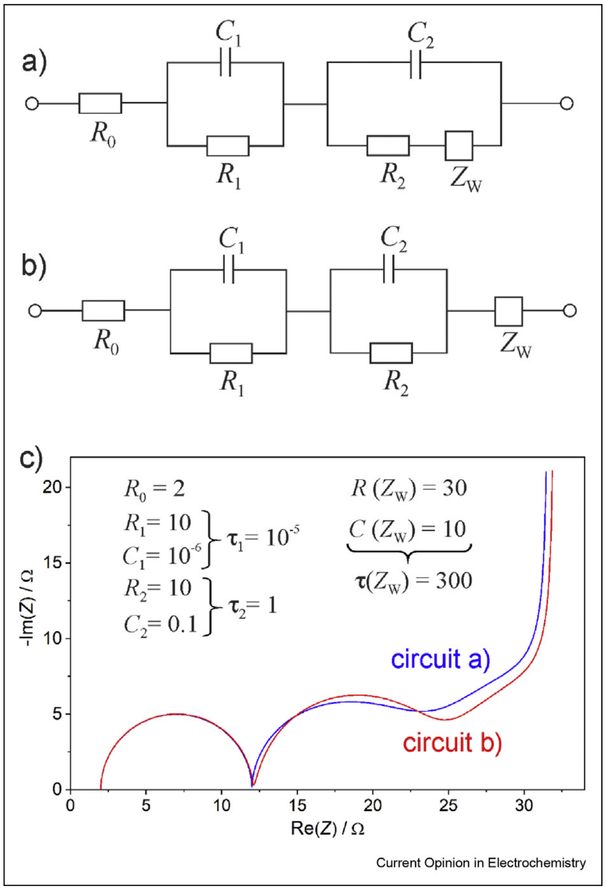
In cases, where the de Levie simplification is intended to be used for analysis of the low-frequency part of impedance spectra (e.g., below ca. 1 Hz), however, a special care is needed. While the de Levie model can describe the solid state diffusion (through Warburg element, Z_w), it does not include other possible diffusional contributions, such as diffusion in the porous part of electrode and in separator (compare Figure 2e,f). All these diffusions can overlap in realistic spectra that have to be taken into account. Occasionally, authors try to compensate for the lack of additional diffusion in electrolyte phases by including additional Warburg element in certain position in the de Levie circuit [16,17]. However, the physical background of such additions is usually unclear. It can be advised that in such more complex cases, the derived full model (Figure 2a) is used instead of its simplifications.

Use of fully simplified circuit models (Figure 2c, d, g, h) for analysis of impedance of porous battery electrodes and cells

As mentioned above, in fully optimized battery electrodes or even whole battery cells, most of the impedance contributions get very small and only a couple of processes prevail in the measured spectra (Figure 2h for half- and 2g for full cell). Although the derived models get very simple (Figure 2c,d), the topology of individual elements remains important if one wishes to get physically sound parameter values, as shown later on.

A typical EIS measurement of contemporary graphite-NMC 18650 cell in a wide frequency range [18] gives a spectrum that resembles very much the theoretical

Figure 3



(**a**) General equivalent circuit based on simplification shown in Figure 2d and used frequently in the literature for description of well-optimized battery cells; (**b**) Alternative to circuit (**a**) which is also used frequently in the literature but with less clear physical background; (**c**) A comparison between the outputs of circuits (**a**) and (**b**) for the case of selected parameters values shown above the graphs. Note that the difference becomes progressively bigger with increasing ratio $\tau(Z_W)/\tau_2$ where $\tau(Z_W) = R(Z_W)\cdot C(Z_W)$ and $R(Z_W)$ and $C(Z_W)$ are the resistance and chemical capacitance connected to Warburg impedance when the latter is modeled as a finite-space Warburg element [9].

case shown in Figure 2h, except that at highest frequencies an inductive line extending to positive values of imaginary impedance (below x-axis) is seen which is due to inductive properties of leads and wound cell geometry. Excluding the inductive part, the authors proposed an equivalent circuit that is almost the same as the one shown in Figure 2d, except that $Z_{W,anode}$ is missing. This leads to the typical circuit shown in Figure 3a used in many recent articles. It should however be noted that while such further simplification can be appropriate, one should nevertheless check whether the diffusion impedance in anode (here graphite) is really negligible compared to the diffusional impedance in NMC. A very similar approach was used in the analysis of graphite—NCA (lithium-nickel-cobalt-aluminum oxide) and silicon-NCA pouch cells [19], in analysis of all-solid-state-batteries [20], or in sodium insertion batteries [21]—to mention only a couple of typical recent examples.

Very frequently, however, the Warburg impedance due to solid state diffusion, Z_W, is taken out of the Randles-like combination with a resistor and a capacitor (Figure 3a, see also Figure 2g,h) and positioned in series with two parallel R–C terms [22–29], as shown in Figure 3b. Sometimes element repositioning facilitates further analyses such as the use of distribution of relaxation times [20]. Although from the physical point of view the change of element topology may be highly questionable, it is also true that in many cases it does not affect the quality of parameter analysis [25*]. Namely, the time constant for the low-frequency process (determined by the rate of diffusion in insertion material) is usually much bigger (e.g., more than ca. 1000 times) than the time constant of the parallel R–C terms. If, however, the ratio between those time constants gets smaller, the spectrum generated by the circuit in Figure 3b starts to deviate significantly from that obtained from derivation (Figure 3a or Figure 2g,h etc.). Thus, it is advised that authors check the degree of coupling of individual sets of elements giving rise to appropriate impedance features prior to using non-derived (intuitive) circuit variants. In any case, it is probably more reasonable to use directly the derived variant in Figure 3a as it allows for the same level of simplicity in analysis of measured spectra.

Conclusions and perspectives

Impedance spectroscopy is a valuable electrochemical tool that can effectively decouple a multitude of electrochemical processes taking place in given system, for example, in a battery cell. Although detailed physics based models of a battery cell predict many impedance features (at least 10 for typical insertion anode-electrolyte-insertion cathode cell), the measurements on realistic battery cells only reveal a couple of arcs or lines in a wide frequency range. We showed systematically how the full theoretical solution represented as a complex transmission line can be gradually simplified into simpler circuit variants and used on practical cases of interest reported in recent literature. Specifically, we underline the benefits of the so-called de Levie simplification which accurately describes the measured spectra from ca. 1 Hz to highest measurable frequencies. We also demonstrated that the usage of further simplifications in which the porous nature of electrodes is neglected may be quite appropriate for well optimized battery cells. However, we also emphasized the importance of correct topology of circuit elements which, if not taken properly into account, may lead to erroneous evaluation of parameter values.

In perspective, it may be expected that the usage of EIS in the field of batteries will see further development in many directions. First, based on recent trends in the literature, one may expect preparation of special cells that enhance insight into particular feature of interest (e.g., tortuosity [30,31], ionic conductivity in porous electrode [14*] etc.). Further, measurement techniques and models that allow monitoring of impedance during cell operation (exploiting the so-called dynamic impedance measurement [32*]) will be further developed and used. Finally, expansion of modeling possibilities from predominantly 1D to 3D structures can also be envisaged [5**].

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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